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ELECTRICAL CONDUCTIVITY  
OF IRRADIATED INSULATING  
ORGANIC LIQUIDS AND GLASSES

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BUDAPEST



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ELECTRICAL CONDUCTIVITY OF IRRADIATED INSULATING ORGANIC  
LIQUIDS AND GLASSES

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## INTRODUCTION

Recently there has been a considerable revival of interest in the ionic aspects of the interaction of ionizing radiations with matter [1-6]. With the use of pulse techniques rate processes of nanosec duration and faster have become accessible for studies and this has resulted in an accumulation of many contradictory data. For example, the measured mobility values of charge carriers produced by irradiation of insulating liquid hydrocarbons cover a range of  $\mu$   $10^2 - 10^{-6}$  cm<sup>2</sup>/volt sec [7,8], thus opening a field for renewed discussions. The same applies for the several theories proposed to explain the observed phenomena of charge generation and recombination.

In this paper the results of studies on the pulsed photoconductivity and d.c. electric conductivity produced in 3-methylpentane /3-MP/ by gamma irradiation are reported. It is hoped that the measured variations of charge carrier mobilities,  $k'/\mu$  values and conductivity with temperature and other parameters presented here will be useful in the interpretation of charge carrier generation, migration and recombination processes.

### Purification of materials and preparation of samples

3-methylpentane /3-MP; Merck/ was purified by shaking with sulfuric acid, and then washing with dilute NaOH solution and distilled water. The 3-MP freed from unsaturated hydrocarbons was distilled by passage through a 120 cm column filled with Rashig rings. The middle fraction was analyzed by gas chromatography.



The cells holding the measured samples were evacuated to  $4 \cdot 10^{-6}$  torr by the conventional freeze-thaw pumping technique. Each sample was vacuum distilled onto a Na mirror by repeated runs until completely dehydrated. The dehydrated sample was then distilled into a cold trap in the sidearm of the cell, which was subsequently sealed off. The electrical conductivity of the sample in the cell was measured as  $\sigma \approx 10^{-17} \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature.

#### Measuring equipment

The conductivity cell was prepared from quartz and where not exposed to the light beam from glass. A circular silver net /T ~ 70%/, 24 mm in diameter, and a highly polished Al disc spaced 7 mm away were used as anode and cathode, respectively. The former was surrounded by a 3 mm wide silver-plated copper ring, which was grounded during the measurements. The temperature was measured by thermocouples located in a 1,5 mm diameter glass tube inserted directly behind the cathode. For measurement the sample was poured from the sidearm into the cell.

The cell was placed into a double-walled cylindrical copper block of 2 cm wall thickness surrounded by helically wound cooling tubes. A hole of the same size as the anode was drilled into the copper block to permit the illumination of the cathode by the light flash. For good heat transfer the space between the cell and the copper walls was filled out with copper chips. The block with the measuring cell was housed in a  $25 \times 25 \times 25$  cm iron box with a quartz window for the exposure of the cell to the light flash. Coaxial shielded cables connected the electrodes to the electrometer and the high voltage supply. Vapour condensation in the iron box was prevented by evacuating it to  $10^{-2}$  torr pressure and introducing dry purified  $\text{N}_2$ . The sample temperature was controlled by varying the liquid nitrogen flow rate in the cooling spiral.

The output current from the anode was measured with a Keithley-type 640 electrometer with an input impedance of  $10^6$  ohm. The electrometer output was observed on an EMG TR-4401 oscilloscope.



The double-walled discharge tube with ring electrodes used for producing the light flashes was built at our laboratory /Fig. 1/. The quartz envelope of the discharge tube was removable to permit the cleaning of the end window from the dust produced by the electrode discharge. Cleaning was required after 30-40 flashes. The discharge tube was connected across a manometer to an argon gas balloon that could be pumped out and refilled at will. During operation the argon pressure of the flash tube was kept at 120 mmHg. A condenser of 4  $\mu$ F capacity charged to 10,5 kV was used as the voltage supply. Random triggering of the discharge tube was prevented by the shaping of the tube which was chosen to be such that self-discharge occurred at 5-7 kV under the applied pressure. A thyatron was inserted into the grounding line of the flash circuit so that the condenser could not discharge across the flash tube unless the thyatron had been triggered by a pulse of 2,5  $\mu$ sec and 200 V. The oscilloscope was triggered simultaneously with the flash by a RCA 931A -type multiplier.

#### Photocurrent measurement

A negative voltage of 1000 to 3500 V was applied to the cathode before exposure of the cell filled with 3-MP or 3-MHx to a light flash of 15  $\mu$ sec duration. The voltage drop caused by the light flash on the measuring resistor of the anode output amplifier was registered by the oscilloscope. The RC time constant of the measuring circuit was 100  $\mu$ sec at an input impedance of  $10^6$  ohm. Depending on the applied field and the sample temperature the photocurrent pulse varied from 0,2 to 5 sec.

#### EXPERIMENTAL RESULTS

Charge carrier mobility and recombination constant,  $k'$ , values were obtained from the curves of current pulse versus time. The form of these varied with the field applied; the two typical extremes are shown in Fig. 2 and 3. The current pulse shape reveals that carriers are generated



uniformly within the cell and that the amount of electrons photoejected from the Al cathode can be neglected. No photocurrent was observed after inserting a filter to cut out light of  $\lambda < 280 \mu\text{m}$ .

The current pulse results from the recombination of electrons and holes and their migration towards corresponding electrodes at velocities of  $\mu_-E$  and  $\mu_+E$ , respectively. Thus the boundaries of the neutral central recombination volume  $V_r$  move toward each other at a speed of  $(\mu_+ + \mu_-)E$  leaving a hetero-space charge layer at both electrodes. The variation in time of the volume  $V_r$  in which recombination takes place is expressed [9,10] by

$$V_r = V \left( 1 - \frac{t}{t_s} \right) \quad /1/$$

where  $V$  is the cell volume and  $1/t_s = 1/t_s^+ + 1/t_s^-$ . The time  $t_s = \frac{d}{(\mu_+ + \mu_-)E}$ , where  $d$  is the electrode separation,  $\mu_+$  and  $\mu_-$  are the positive and negative charge carrier mobilities and  $E$  is the applied electric field. The charge carrier density inside  $V_r$  due to second order recombination is given by

$$n = \frac{n_0}{1 + n_0 k' t} \quad /2/$$

where  $n_0$  is the initial concentration of the charge carriers and  $k'$  is the recombination constant. The total charge collected on the anode caused by the movement of negative carriers is [10]

$$Q_c^- = \frac{V_e}{T_s^-} \left[ \int_0^{t_s} \frac{n_0 [1 - (t/t_s)]}{1 + k' n_0 t} dt + \int_0^{t_s} \frac{1}{t_s k'} \ln \left( \frac{1 + k' n_0 t}{1 + k' n_0 t (t_s/t_s^-)} \right) dt + \right. \\ \left. + \int_{t_s}^{t_s^-} \frac{1}{t_s k'} \ln \left( \frac{1 + k' n_0 t_s}{1 + k' n_0 t t_s/t_s^-} \right) dt \right] \quad /3/$$



where  $n_o = G_{fi} D/100$ ,  $G_{fi}$  is the free ion yield, and  $D$  the dose delivered in a pulse. Analogous expression can be written for  $Q_c^+$  by substituting  $t_s^+$  for  $t_s^-$  in Equ. 3. The collected total charge, i.e. the charge which can be obtained from the area under a current pulse, is

$$Q_c = Q_c^- + Q_c^+ = \frac{Ve}{t_s k'} \ln 1 + k'n_o t_s \quad /4/$$

At low fields when  $1/k'n_o = t_{1/2} \ll t_s$  and  $t \ll t_s$  recombination dominates and the current is

$$i = \frac{Ve}{t_s} \left( \frac{n_o}{1+k'n_o t} \right) \quad /5/$$

At high fields  $t_s \ll t_{1/2}$  and the pulse shape is determined by the mobilities of the charge carriers, which give triangular-like current vs time curves. The total number of recombined charges of one sign in a given pulse is [9]

$$N = \int_0^{t_s} k'n^2 V_r dt = n_o V \left[ 1 - \left( 1/t_s n_o k' \right) \ln(1+k'n_o t_s) \right] \quad /6/$$

Charge carrier mobilities were calculated from current vs time curves of the type shown in Fig. 3 using the formula  $\mu = t_s/dE$ , the value  $t_s$  being obtained as the time corresponding to the knee of the curves. The variation of  $\mu_+ + \mu_-$  as a function of temperature is shown in Fig. 4.

An important constant governing the recombination of the charge carriers is  $k'$ , the recombination coefficient. Providing that the probability of recombination is  $1/e$  if the thermal kinetic energy of a negative charge equals that of the Coulombic attraction of a positive hole [i.e.  $3/2 kT = e^2/\epsilon r_o$ ], in other words the reaction radius is  $r_o = 2e^2/3\epsilon kT$ , then the recombination rate constant is [9,11,12]



$$k' = \frac{8\pi e(\mu_+ + \mu_-)}{3\epsilon} \quad \text{or simply} \quad \frac{4\pi e\mu}{\epsilon} \quad /7/$$

Formula /7/ is valid only if  $\lambda \ll r_0$ , where  $\lambda$  is the mean scattering free path of the charge carriers. The value of  $k'/\mu$  can be evaluated from the slope of the curves of  $1/i$  vs time, which are straight lines if recombination dominates during the current pulse lifetime. Typical curves derived from photocurrent pulses and from curves obtained after interruption of  $^{60}\text{Co}$  gamma irradiation are shown in Fig. 5. In Fig. 6 the variation of  $k'$  obtained from  $k'/\mu$  values by substituting the measured  $\mu$  values can be seen.

If the viscosity values measured by Willard et al. [13] and in this laboratory are used /see Fig. 7/, the product of mobility and viscosity,  $\mu\eta$ , remains constant down to  $T = 170^\circ\text{K}$  but deviates considerably at lower temperatures.

For the interpretation of the initial photocurrent vs temperature curve /Fig. 8/ we assumed that this exponential temperature dependence was connected with an intrinsic charge carrier-generation mechanism. Instead of calculating an activation energy the measured currents were interpreted as varying with temperature according to  $\exp(-T_0/T)$ , where  $T_0 = 2e^2/3\epsilon k\lambda$ . Calculation shows that at room temperature  $r_0/\lambda$  is approximately 7,4 increasing to 28,4 at  $77^\circ\text{K}$ .

It is worth noting that the activation energies calculated from the curves of  $\log \sigma$  vs  $1/T$  obtained with unirradiated and gamma-irradiated samples differ markedly. It appears possible that the temperature dependence of dark conduction of saturated hydrocarbons reflects the temperature dependence of electrode processes, whilst processes taking part in the bulk of the liquid determine the temperature dependence of  $\sigma$  in irradiated materials.



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## FIGURE CAPTIONS

- Fig. 1 Experimental arrangement for pulsed-light conductivity measurements  
A amplifier, O oscilloscope, T thermostate, FT flash-tube, IG pulse generator, C condensers, HVS high voltage supplies.
- Fig. 2 A typical pulse of current versus time in 3-MP at low fields.  
Each major division on the vertical scale corresponds to  $5 \times 10^{-10}$  A and each division on the horizontal scale to 0.1 sec. The electric field strength was 2 kV/cm,  $T = 293^{\circ}\text{K}$
- Fig. 3 Typical curves of current pulse versus time in 3-MP at high fields.  
a/ The vertical scale is  $3 \times 10^{-11}$  A/major division and the horizontal scale is 0,5 sec/major division. The electric field strength was 3 kV/cm.  $T = 223^{\circ}\text{K}$ .  
b/ The vertical scale is  $1,5 \times 10^{-12}$  A/major division, the horizontal scale is 2 sec/major division.  $E = 4,6$  kV/cm,  $T = 148^{\circ}\text{K}$ .
- Fig. 4 Temperature dependence of the mobility of charge carriers generated in 3-MP by a pulse of light.
- Fig. 5 Reciprocal curves of current versus time for photoionized and  $^{60}\text{Co}$  gamma irradiated 3-MP. 1- $\gamma$ -irr.,  $T = 295^{\circ}\text{K}$ ,  $E = 16,2$  kV/cm.  
2- $\gamma$ -irr.,  $T = 295^{\circ}\text{K}$ ,  $E = 4,45$  kV/cm, 3-photon,  $T = 295^{\circ}\text{K}$ ,  $E = 1,6$  kV/cm, 4-photon i,  $T = 263^{\circ}\text{K}$ ,  $E = 1,6$  kV/cm.
- Fig. 6 Temperature dependence of  $k'$  in 3-MP. 1- $\gamma$  irradiation, 2-photo excitation
- Fig. 7 Temperature dependence of viscosity /poises/ for 3-MP;  
a/ this work,  
b/ A.C. Ling and J.E. Willard [13]
- Fig. 8 Curve of initial photocurrent vs reciprocal temperature for 3-MP.



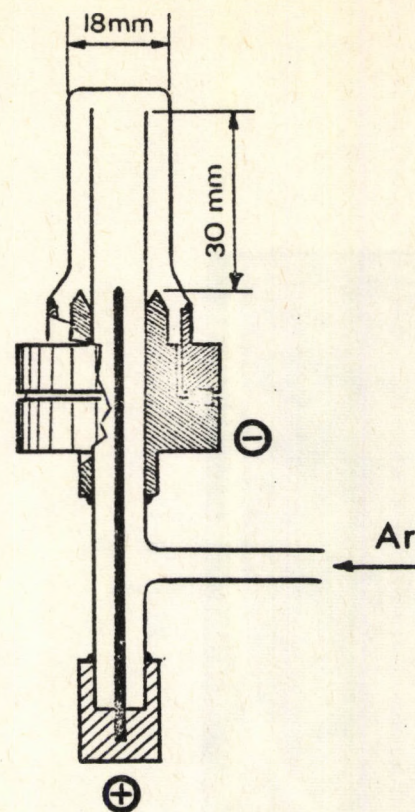
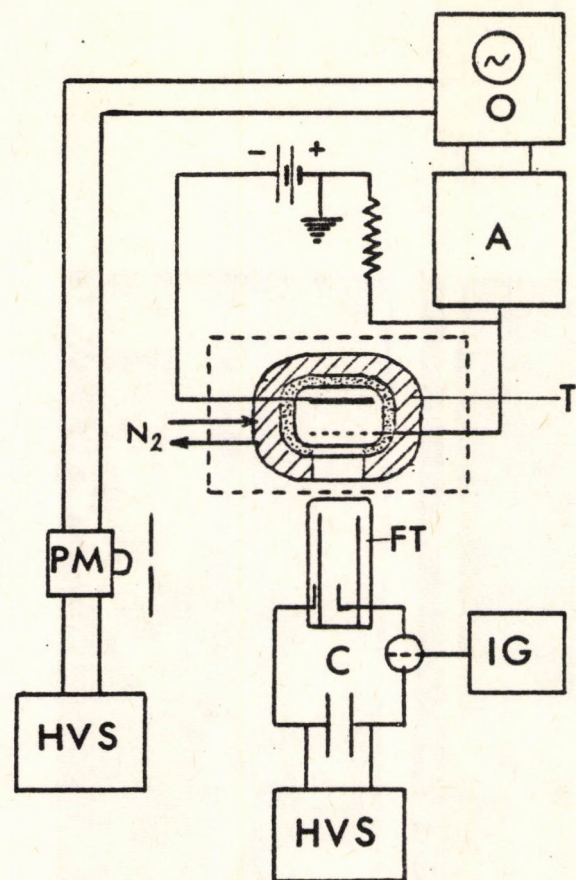


Fig. 1



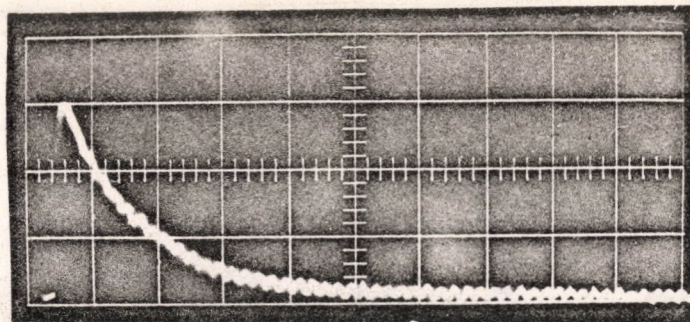


Fig. 2

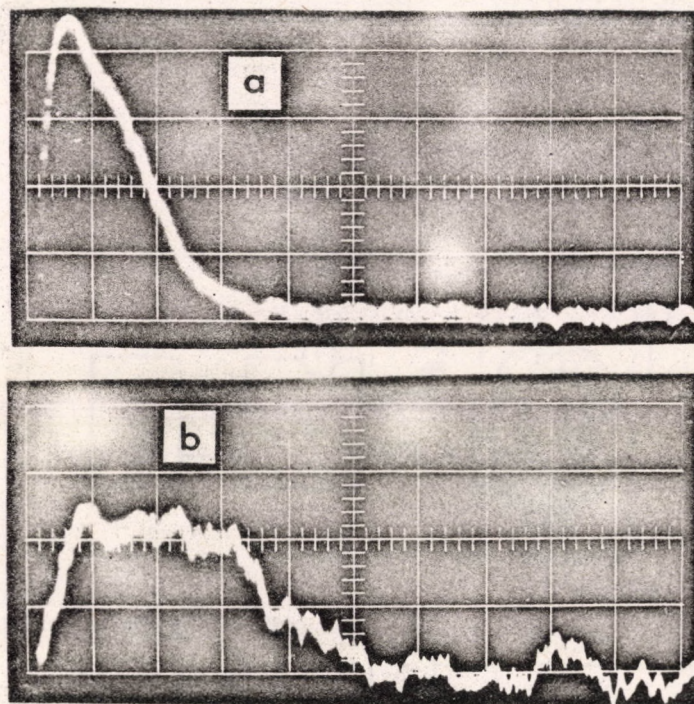


Fig. 3



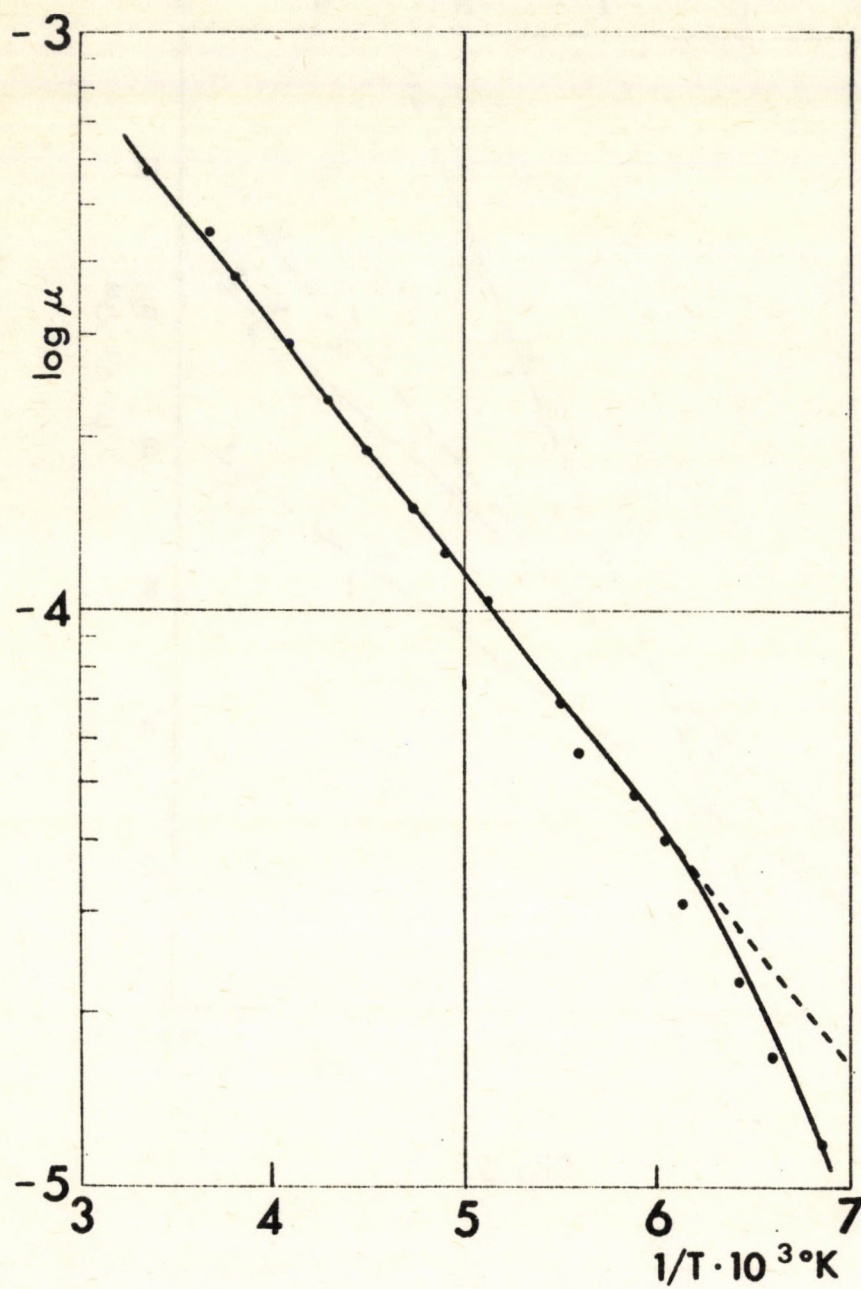


Fig. 4



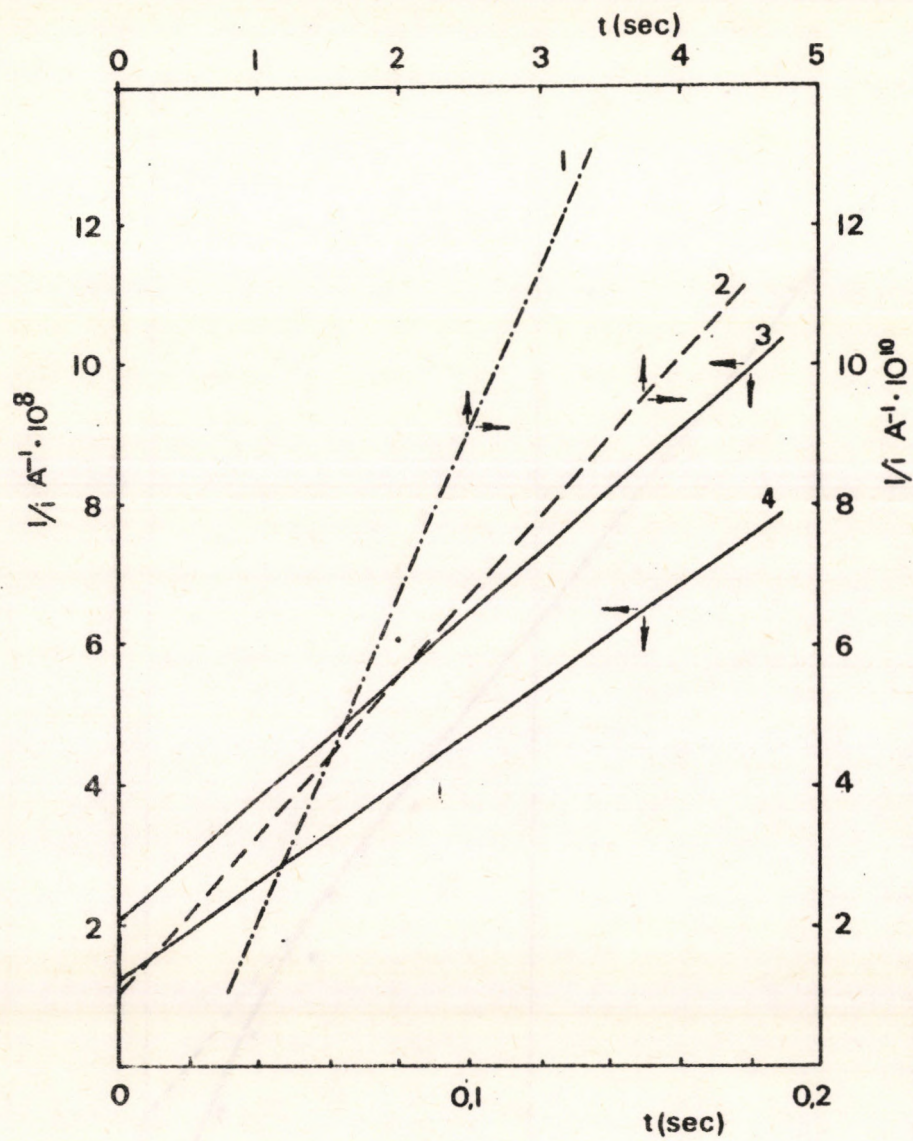


Fig.5



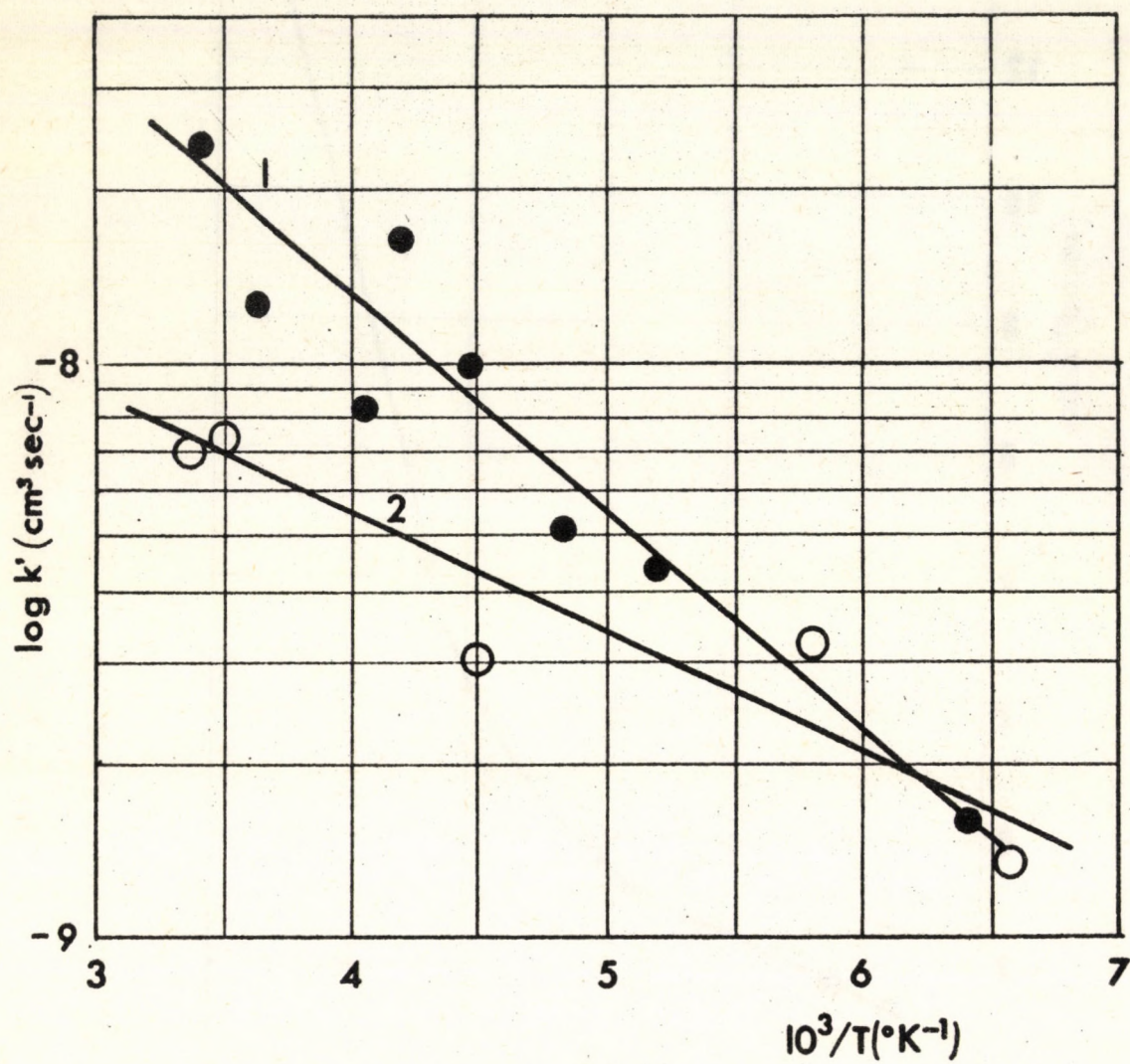


Fig.6



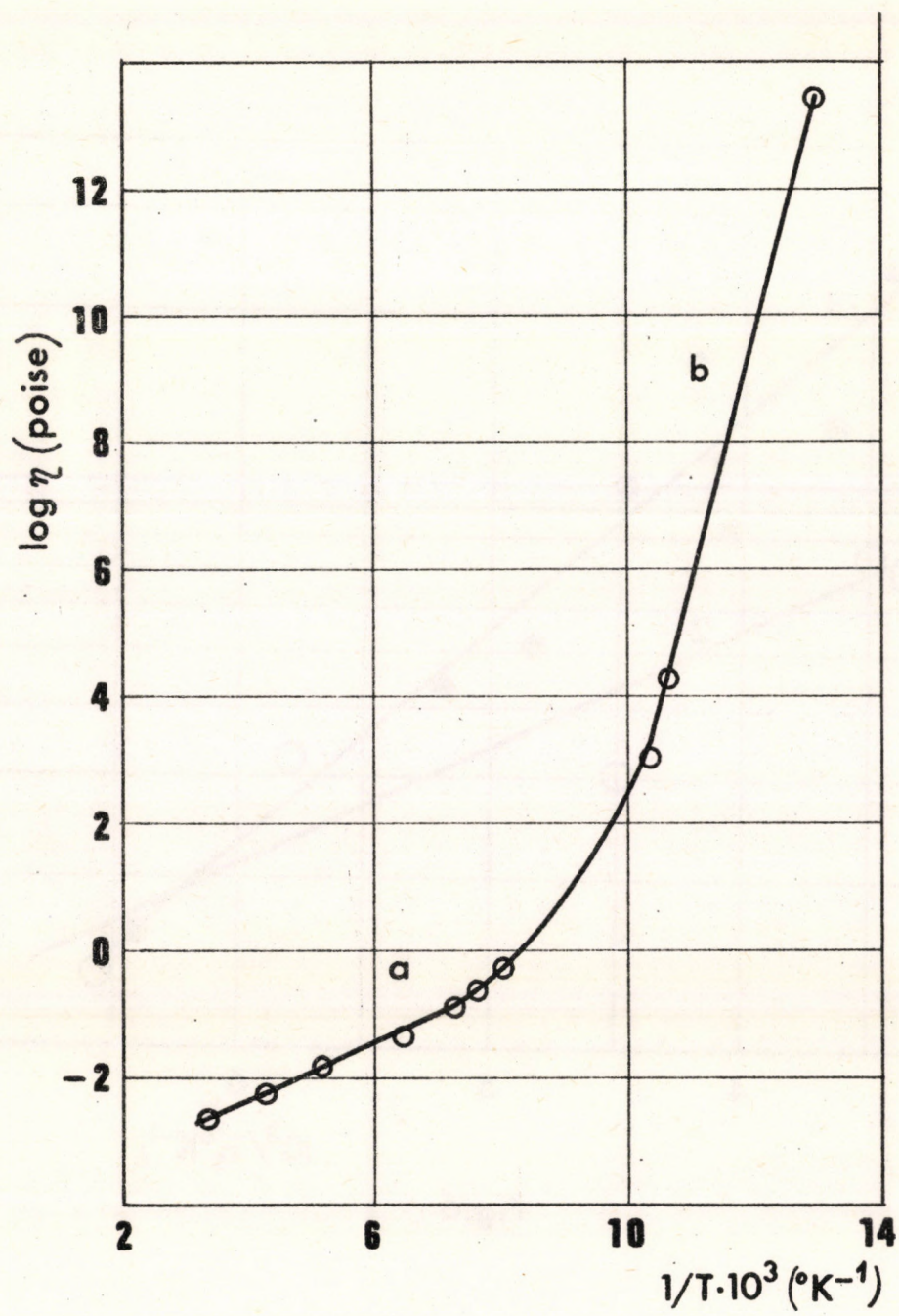


Fig.7



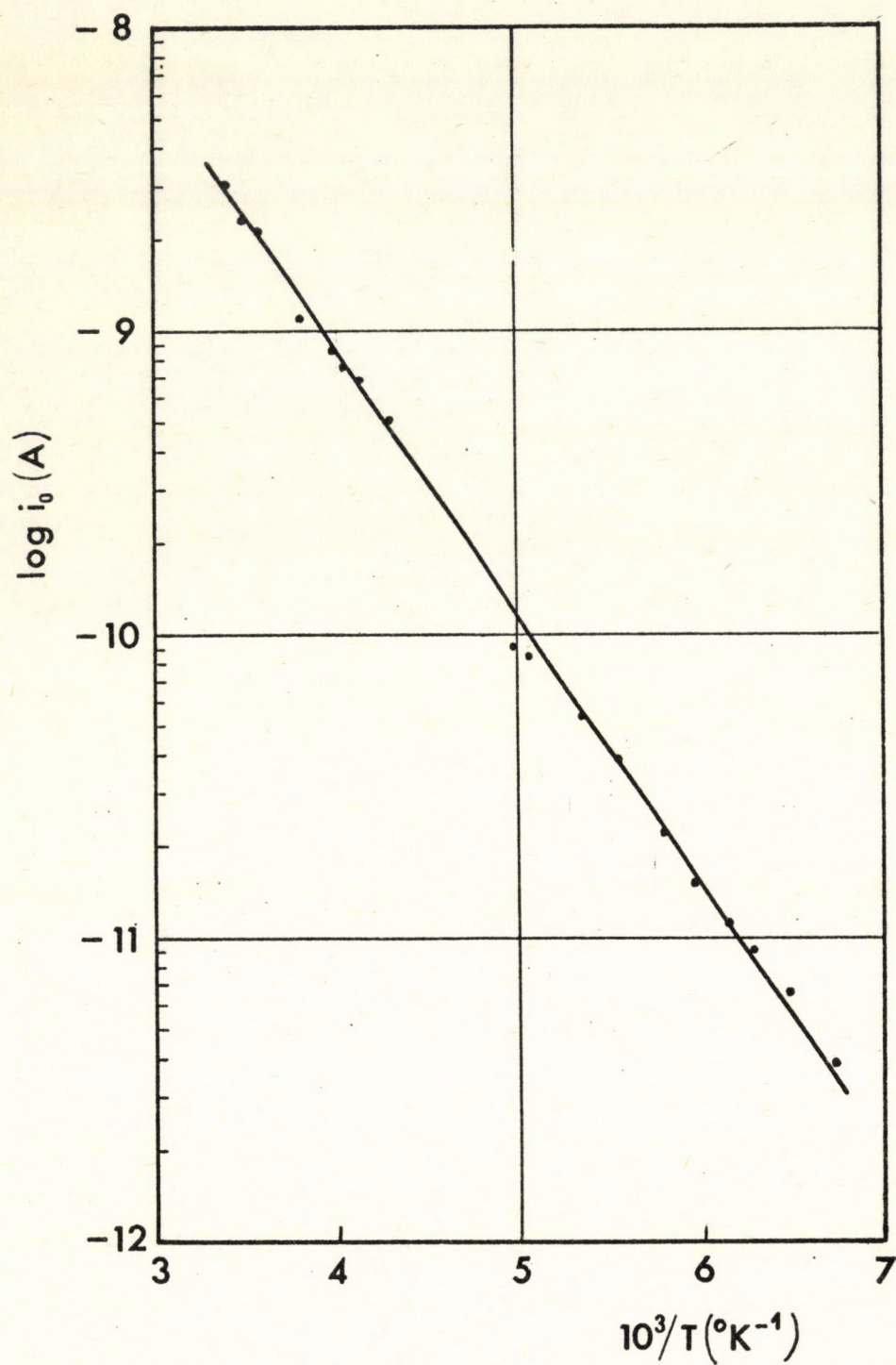


Fig.8











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